DOI: 10.22607/IJACS.2017.502001

Available online at www.ijacskros.com

Indian Journal of Advances in Chemical Science

Indian Journal of Advances in Chemical Science 5(2) (2017) 76-80

Adsorption of Lead and Zinc on *Curcuma longa* Leaf Powder from Aqueous Solutions

K. Subbarayudu[1], R. Prathibha[1], C. Narasimha Rao[1], K. Sivakumar[2], P. Venkateswarlu[1]*

[1]Department of Chemistry, S. V. University, Tirupati - 517 502, Andhra Pradesh, India. [2]Department of Chemistry, S. V. Arts College, Tirupati - 517 502, Andhra Pradesh, India.

Received 09th January 2017; Revised 19th March 2017; Accepted 20th March2017

ABSTRACT

In this paper, adsorption of lead and zinc on Curcuma longa leaf powder from solutions with environmentally relevant concentrations of metals was studied. The kinetics of adsorption of metal ions was analyzed. Optimum pH values for maximum metal ion adsorption were determined. Adsorption isotherms were expressed by Langmuir and Freundlich models. Langmuir adsorption model fits the experimental data reasonably well than Freundlich model. The thermodynamic parameters - such as standard Gibb's free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) - were evaluated, which indicated that this system was spontaneous and endothermic. The studies showed that this low-cost material could be used as an efficient adsorbent for the removal of lead and zinc from aqueous solutions.

Key words: *Curcuma longa leaf powder, Adsorption, Lead, Zinc, Kinetics, Thermodynamics.*

1. INTRODUCTION

Heavy metals are used in several industrial applications due to their useful technological attributes. Although many heavy metals are necessary in small amounts for the normal development of the biological cycles, most of them become toxic at high concentration [1]. The waste water discharged from these industries cause toxic metal concentration of surface, sea and ground water resources, and enter the food chain of humans and other forms of life. Heavy metals being non-biodegradable tend to accumulate in living organisms, thus becoming a permanent source of hazard to health and life [2-5]. Heavy metals in aqueous solutions are usually removed by various remedial technologies such as adsorption, ion exchange, coagulation, floatation, chemical precipitation, and reverse osmosis [6-9]. Biosorption is a biological method and can be an alternative to conventional wastewater treatment facilities [10,11].

In this work, *Curcuma longa* leaf powder is utilized as biosorbent to remove lead and zinc ions from aqueous solutions.

C. longa is a rhizomatous herbaceous perennial plant belongs to *Zingiberaceae* family and native to Indian subcontinent. Its rhizome is used as herbal medicine and its leaves are almost do not have any economic value after separating from plant. Hence, in this study, a biosorption method for the removal of lead and zinc ions using *C. longa* leaf powder as low-cost biosorbent has been developed.

2. EXPERIMENTAL

2.1. Preparation of C. longa Leaf Powder

The leaves were washed thoroughly with tap water followed by deionized water, and the leaves were sundried and crushed to fine powder by a high-speed rotary cutting mill. A weighed amount (50 g) of *C. longa* leaf powder was transferred into 1000 ml glass beaker and added 500 ml of deionized water. The resulting mixture was stirred for 1 h and the biosorbent was separated from the solution by filtration, washed with distilled water several times until no color was detected in the filtrate. Afterward, it was dried in an oven at 70°C for 24 h and kept in a desiccator until it reaches room temperature and packed in polythene cover for further studies. The resulting biomass was designated as *Curcuma longa* leaf powder (CLLP) for further representation.

2.2. Preparation of Solutions

Lead and zinc solutions of desired concentration were prepared by dissolving the appropriate amounts of $Pb(NO_3)_2$ and $ZnSO_4.7\ H_2O$ (Merck) in distilled water. The pH of each test solution was adjusted to the

*Corresponding Author:
E-mail: pvprofvenkat51@gmail.com
Phone: +919393600444

required value with 0.1 N NaOH or 0.1 N HCl. All the chemicals used in this study were of analytical grade.

2.3. Batch Adsorption Experiments

Adsorption capacity of CLLP was studied by adding 0.1-0.7 g of adsorbent in 100 ml of lead and zinc solutions at different concentrations. The flasks were sealed with glass stopper and kept on oscillating shaker; they are shaken for 140 min at 160 rpm. To study the effect of different factors that are affecting the adsorption such as of lead and zinc, effect of pH, effect of contact time, a series of batch experiments were conducted with different initial concentration of lead and zinc solutions (50, 75, 100, 125 mg L^{-1}). Then, the conical flasks were put on to the oscillating shaker for 140 min to reach adsorption equilibrium at the fixed shaking speed (160 rpm), then the concentration of lead and zinc in the filtrate was determined.

3. RESULTS AND DISCUSSION

3.1. Scanning Electron Microscope (SEM) Analysis

Figure 1 shows the SEM micrographs of CLLP before and after adsorption. From these images, it is clear that CLLP has porous and rough surface texture, where there is a good possibility for the adsorption of lead and zinc. However, it is clearly shown that the surface of CLLP is covered with a layer of lead and zinc after adsorption.

3.2. Effect of Contact Time

The effect of contact time on the extent of adsorption of lead and zinc at different initial concentration of metal ions was investigated. The biosorption yield of lead and zinc increased considerably until the contact time reached 140 min. Further increase in contact time did not enhance the adsorption. Hence, the optimum contact time was selected as 140 min for further experiments.

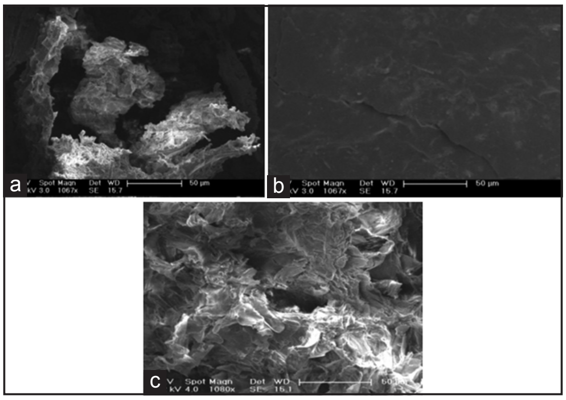

Figure 1: (a) Scanning electron microscope (SEM) image of *Curcuma longa* leaf powder before adsorption, (b) SEM image of *C. longa* leaf powder after adsorption of lead, (c) SEM image of *C. longa* leaf powder after adsorption of zinc.

3.3. Effect of pH

The effect of pH on the adsorption of lead and zinc by the CLLP was studied in the pH range 2.0-6.0. The maximum bioadsorption was observed at pH 6.0 and 5.5 for lead and zinc, respectively. The adsorption could not be carried out beyond pH 6.0 due to precipitation of $Pb(OH)_2$ and $Zn(OH)_2$. At low pH, the hydronium ions concentration is more hence these are bound to the adsorbent leaving the metal ions unbound. When pH value is increased, the concentration of hydronium ions decreased and the metal ions are adsorbed on the adsorbent.

3.4. Kinetic Studies

Kinetic studies were carried out to study pseudo-first order and pseudo-second order and intraparticle diffusion models. The pseudo-first order rate equation is [12],

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (1)$$

Where, q_e and q_t are the amount of metal ion adsorbed on adsorbent (mg/g) at equilibrium and at t time, respectively, and K_1 is the rate constant of first-order adsorption (min^{-1}). Pseudo-second-order rate equation can be expressed as [13,14],

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Where, K_2 is the rate constant of second order adsorption (g/mg min). The plots are shown in Figures 2 and 3.

The equation corresponds to intraparticle diffusion model is expressed as [15],

$$q_t = K_{id} t^{0.5} + C \quad (3)$$

In Figures 4 and 5, the initial covered region corresponds to the external surface obtained, the second region relates the gradual uptake indicating intraparticle diffusion as the rate limiting step and final region indicates the equilibrium uptake. The values of rate constants and correlation coefficients of kinetic studies are shown in Table 1. Compared to pseudo-first order and intraparticle diffusion kinetic model, a good correlation coefficient was obtained for pseudo-second order, which indicates that the biosorption follows pseudo-second order rate expression.

3.5. Equilibrium Studies

The empirical Freundlich equation based on adsorption on a heterogeneous surface is [16],

$$q_e = K_f \left(C_e\right)^{\frac{1}{n}} \quad (4)$$

Where, q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/L), K_f and

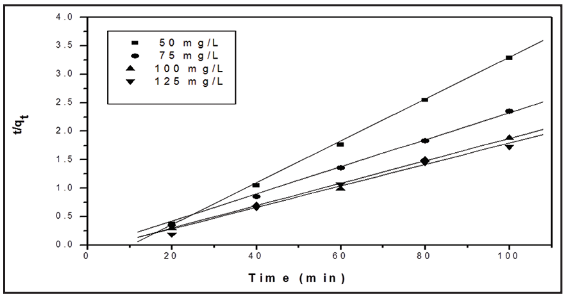

Figure 2: Pseudo second order kinetic plots at different initial concentrations of lead on *Curcuma longa* leaf powder.

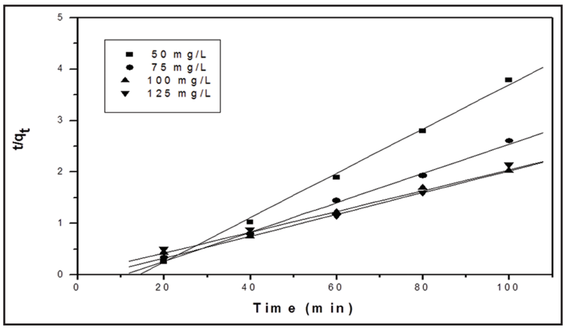

Figure 3: Pseudo second order kinetic plots at different initial concentrations of zinc on *Curcuma longa* leaf powder.

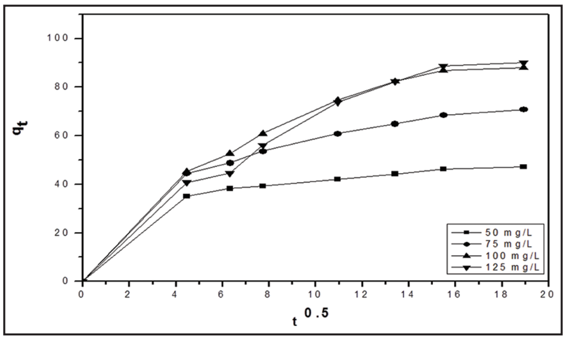

Figure 4: Weber-Morris plots at different initial concentrations of lead on *Curcuma longa* leaf powder.

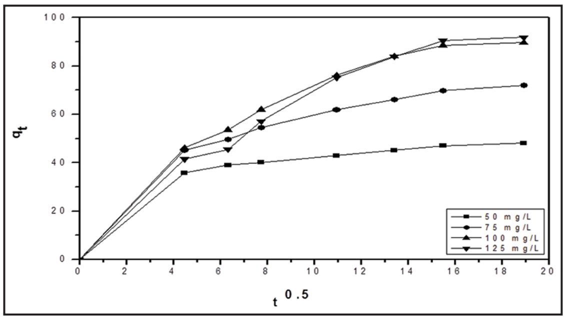

Figure 5: Weber-Morris plots at different initial concentrations of zinc on *Curcuma longa* leaf powder.

Table 1: Adsorption rate constants of pseudo-first order, pseudo-second order model and Weber-Morris model for lead and zinc on CLLP.

Initial concentration of metal ion (mg/L)	Pseudo first-order model				Pseudo-second order model				Weber-Morris model			
	Pb(II)		Zn(II)		Pb(II)		Zn(II)		Pb(II)		Zn(II)	
	K_1 (min^{-1})	R^2	K_1 (min^{-1})	R^2	K_2 ([g/mg] min)	R^2	K_2 ((g/mg)min)	R^2	K_{id} ([mg/g] $min^{-0.5}$)	R^2	K_{id} ([mg/g] $min^{-0.5}$)	R^2
50	0.0502	0.945	0.0442	0.953	0.0023	0.997	0.0015	0.999	0.8962	0.979	1.1004	0.971
75	0.0507	0.901	0.0540	0.918	0.0015	0.994	0.0009	0.997	1.3149	0.988	1.7206	0.974
100	0.0503	0.952	0.0548	0.912	0.0011	0.994	0.0007	1.000	1.6951	0.974	2.1463	0.973
125	0.0596	0.961	0.0546	0.926	0.0016	1.000	0.0010	0.999	1.5902	0.953	2.0680	0.950

CLLP=Curcuma longa leaf powder

Table 2: Parameters of Langmuir and Freundlich isotherms and thermodynamic parameters for adsorption of lead and zinc onto CLLP.

Metal ion	Temperature (K)	Langmuir constants			Freundlich constants			ΔG° (kJ/mol)	ΔS° (J/mol K)	ΔH° (kJ/mol)
		Q_0 (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	1/n	R^2			
Pb(II)	303	35.89	0.1703	1.000	9.520	0.349	0.987	-37.68	0.156	9.58
	308	35.97	0.1794	1.000	9.778	0.346	0.987	-38.43		
	313	35.70	0.1924	0.999	10.059	0.340	0.988	-39.24		
Zn(II)	303	38.78	0.2253	0.993	12.065	0.314	0.952	-38.03	0.159	10.25
	308	38.45	0.2456	0.993	12.455	0.307	0.953	-38.88		
	313	38.38	0.2565	0.993	12.686	0.304	0.952	-39.62		

CLLP=*Curcuma longa* leaf powder

n are equilibrium constants indicating the adsorption capacity and adsorption intensity, respectively.

Equation (4) can be linearized in logarithmic form as given below,

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (5)$$

The Langmuir equation has the form [17],

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (6)$$

Where, q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/L). Q_0 and b are Langmuir constants indicating adsorption capacity and energy, respectively. By plotting $1/C_e$ versus $1/q_e$, the value of b can be determined from the straight line obtained. The constants Q_0 and K_L are tabulated in Table 1.

From the correlation coefficient values of Langmuir and Freundlich models, it is found that the adsorption of lead and zinc best fits to Langmuir model.

3.6. Thermodynamic Studies

The effect of temperature was studied in the range of 303-313 K. The Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) for the adsorption process were obtained using the following equations.

$$\Delta G° = -RTl_nK_c \qquad (7)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (8)$$

$$\ln K_c = \frac{"S^0}{R} - \frac{"H^0}{RT} \qquad (9)$$

Where, T is the temperature in Kelvin, R is the gas constant (8.314 J/mol K), K_c is the equilibrium constant. The enthalpy change (ΔH°) and the entropy change (ΔS°) can be calculated from a plot of ln K_c verses $\frac{1}{T}$ (not shown), and the values are presented in Table 2.

Values of free energy changes ΔG° are negative confirming that adsorption is spontaneous and thermodynamically favorable. The more negative values of ΔG° indicate a higher driving force to the adsorption process. The positive values of ΔH° indicate that the adsorption process is endothermic in nature. The positive values of ΔS° indicate the stability of adsorption process without any structural change at solid-liquid interface.

4. CONCLUSION

The results of this study show that the *C. longa* leaf powder has suitable adsorption capacity with regard to the removal of lead and zinc from aqueous solution. The adsorption process follows pseudo-second-order kinetics and obeyed Langmuir adsorption isotherm. The negative values of ΔG° indicate adsorption is spontaneous and positive values of ΔH° and ΔS° were calculated and concluded the adsorption process was endothermic.

5. REFERENCES

1. A. Dursun, K. Yudrakok, S. S. Yalcin, G. Tekinalp, O. Aykut, G. Orhan, G. Morgil, (2016) Maternal risk factors associated with lead, mercury and cadmium levels in umbilical cord blood, breast milk and newborn hair, ***The Journal of Maternal-Fetal and Neonatal Medicine*, 29(6):** 954-961.
2. P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla, D. J. Sutton, (2012) Heavy metal toxicity and the environment, **EXS, 101:** 133-164.
3. J. E. Saunders, B. G. Jastrzembski, J. C. Buckey, D. Enriquez, T. A. MacKenzie, M. R. Karagas, (2013) Hearing loss and heavy metal toxicity in a Nicaraguan mining community: Audiological results and case reports, **Audiology and Neurotology, 18(2):** 101-113.
4. S. Y. J. Mercury, R. S. Hoffman, M. A. Howland, N. A. Lewin, L. S. Nelson, L. R. Goldfrank, (2015) **Goldfrank's Toxicologic Emergencies**, 10th ed. New York, NY: McGraw-Hill Education. p1334-1344.
5. P. A. Meyer, M. J. Brown, H. Falk, (2008) Global

approach to reducing lead exposure and poisoning, ***Mutation Research,*** **659(1-2):** 166-175.
6. O. S. Ayanda, F. A. Adekola, A. A. Baba, B. J. Ximba, O. S. Fatoki, (2013) Application of cyanex extractant in cobalt/nickel separation process by solvent extraction, ***International Journal of Physical Sciences,*** **8(3):** 89-97.
7. G. J. Rincon, E. J. L. Motta, (2014) Simultaneous removal of oil and grease, and heavy metals from artificial bilge water using electro coagulation/flotation, ***Journal Environtal Management,*** **144:** 42-50.
8. F. Fu, L. Xie, B. Tang, Q. Wang, S. Jiang, (2012) Application of a novel strategy-advanced fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater, ***Chemical Engineering Journal,*** **189-190:** 283-287.
9. Z. Liu, F. Liu, S. Wu, X. Wang, Y. Lei, (2013) Removal of Phosphorous and Nickel from an Automobile Waste Water by Coagulation/Flocculation Combined with Magnetite, ***International Conference on Remote Sensing, Environment and Transportation Engineering (RSETE)***.
10. T. A. H. Nguyen, H. H. Ngo, W. S. Guo, J. Zhang, S. Liang, Q. Y. Yue, Q. Li, T. V. Nguyen, (2013) Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater, ***Bioresource Technology,*** **148:** 574-585.
11. R. Gowda, A. G. Nataraj, N. M. Rao, (2012) Coconut leaves as a low cost adsorbent for the removal of nickel from electroplating effluents, ***International Journal of Scientific and Engineering Research,*** **2:** 1-5.
12. S. Lagergren, (1898) About the theory of so-called adsorption of soluble substances, ***Handlingar,*** **24(4):** 1-39.
13. Y. S. Ho, (2004) Citation review of lagergren kinetic rate equation on adsorption reactions, ***Scientometrics,*** **59(1):** 171-177.
14. Y. S. Ho, G. McKay, (1998) Sorption of dye from aqueous solution by peat, ***Chemical Engineering Journal,*** **70(2):** 115-124.
15. W. J. Jr. Weber, J. C. Morris, (1963) Kinetics of adsorption on carbon from solution, ***Journal of the Sanitary Engineering Division, ASCE,*** **89(2):** 31-59.
16. H. M. F. Freundlich, (1906) Freundlich, (1906) Over the adsorption in solution, ***Journal of Physical Chemistry,*** **57A:** 385-370.
17. I. Langmuir, (1918) The adsorption of gases on plane surfaces of glass, mica and platinum, ***Journal of American Chemical Society,*** **40(9):** 1361-1403.

***Bibliographical Sketch**

Prof. P. Venkateswarlu has more than 30 years of teaching and research experience in the Department of Chemistry, S. V. University, Tirupati. He guided 15 Ph.D. students. He has more than 115 publications in internationally reputed journals which are indexed in Science Citation Index. He is the reviewer for many Elsevier journals.